# Methanol production from synergistically integrated natural gas reforming and biomass gasification

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*Abstract*— Low carbon liquid fuels are needed for maritime shipping and long-haul trucking which are difficult to decarbonize by use of battery energy storage or hydrogen. Thermochemical conversion of biomass to liquid fuel (BTL) is a promising option to produce carbon-neutral liquid fuel. However, no commercial BTL plants are yet operating and one of the main reasons is the cost of produced fuel. Here we propose two processes in order to improve the economic appeal of BTL process for producing methanol. These processes employ natural gas as a swing fuel and utilize the synergy between natural gas reforming and biomass gasification. Through this integration, we can use the synergistic effects of adding $H_2$-rich syngas ($H_2$/CO mixture) from natural gas to carbon-rich syngas from biomass to produce the right $H_2$/CO ratio for methanol synthesis while maintaining a high carbon utilization. The biomass syngas generation step in both designs is the same and utilize the illustrative example of an entrained flow gasifier (EFG) with subsequent cleaning of the generated syngas to remove $H_2S$, dust, soot, etc. The differentiating feature of these processes is the syngas generation step from natural gas. In the first design, an autothermal reformer (ATR) is used to generate syngas, while the $O_2$ required for both biomass gasification and natural gas reforming is provided by a solid oxide electrolysis cell (SOEC). The $H_2$ stream from the SOEC is used to adjust the stoichiometry of the methanol synthesis reactor. In the second design, natural gas is sent to a gas-heated-reformer (GHR) followed by an ATR. The heat required in the GHR is provided by the exhaust stream from the ATR, which is the best method to utilize the high temperature exergy of the exhaust stream. The reformed gas has high hydrogen content, but not enough to have the correct stoichiometric number prior to the methanol synthesis. Therefore, a fraction of the reformed gas is sent to a water gas shift (WGS) reactor followed by a $CO_2$ capture unit. The produced stream is used to adjust the stoichiometric number prior to the methanol synthesis reactor. The flexibility and economics of the two processes are compared to a stand-alone BTL process. While the produced methanol includes some fossil carbon, the synergy of this integration and added flexibility would increase the economic viability of deployment of biomass-based fuel production.

*Keywords*— *renewable fuel, methanol, biomass gasification, natural gas reforming*

## I. INTRODUCTION

Low carbon liquid fuels are needed for transportation and other difficult to electrify sectors. Biomass is a renewable carbon source which hold great promise for generating clean low-carbon fuel. However, the carbon conversion efficiency of the conventional Biomass-to-Liquid (BTL) process is low because biomass is hydrogen-lean and its generated-syngas (that is a mixture of $H_2$ and CO) is hydrogen deficient. Carbon conversion efficiency is important because of biomass resource limitations. In this work, we have examined two process configurations to significantly improve carbon conversion efficiency by optimal utilization of both carbon and hydrogen from biomass and natural gas. Syngas from natural gas reforming is rich in hydrogen. Through synergistic integration of syngas from biomass and natural gas, the right composition for methanol synthesis can be produced without much loss of carbon (which is released as $CO_2$) while minimizing the use of fossil carbon. The end goal is to produce methanol, which is an important chemical feedstock and a high-octane fuel. Methanol process is simpler compared to Fischer-Tropsch process which is used for producing jet fuel, diesel, etc..

## II. WHERE TO ADD NATURAL GAS

The choice of introducing natural gas in the process is a very important design consideration. There are **two** general approaches: one is co-feeding of natural gas and biomass to the gasifier, and the second one is parallel natural gas reforming and gasification. The **first** approach, co-feeding of natural gas and biomass in the gasifier has been investigated in the literature (for example [1], [2]). There are challenges to this approach. Due to faster kinetics of $H_2$ reaction compared to other fuels in the gasifier, the $H_2$/CO ratio of the generated syngas would not be high enough for methanol synthesis. Moreover, gas cleaning would be more difficult because of increased flowrates which dilute the biomass impurities with natural gas syngas. Another important point is that methanol production would be coupled to both natural gas and biomass. Therefore, if there is any disruption in supply of either biomass or natural gas, the plant would need to shut down.

In the **second** approach parallel reforming and gasification is employed. This combination has the following advantages: increased feed flexibility as a result of gasification and reforming processes being fully decoupled, with natural gas being used as swing fuel. This enables the plant to continue operating even if either biomass or natural gas supply is disrupted. More importantly, the right $H_2/CO$ ratio for the methanol production can be produced without much loss of carbon, or in other words, the carbon efficiency is significantly increased. Here the techno-economic analysis of integrated parallel reforming of natural gas and biomass gasification to methanol is performed. It is also shown that the carbon efficiency is significantly increased as a result of this integration.

## III. THE PROCESS CONCEPTS

Aspen HYSYS® V12 is used to simulate the process with Peng-Robinson as the thermodynamic model in this study. The properties of the natural gas and biomass feedstocks are shown in Table 1 and Table 2. Two novel designs are investigated for parallel integration of gasification and reforming. For both designs the amount of biomass and natural gas fed to the processes are kept constant, meaning that thermal input from natural gas and biomass kept constant at 134.1 MW. This value is chosen because our aim is to have more than 50% of carbon entering the plant to be from biomass.

TABLE 1: SPECIFICATIONS OF THE NATURAL GAS FEED

| Temperature [°C] | 50 |
|---|---|
| Pressure [bar] | 40 |
| Molar flow [kmol/h] | 350 |
| Mole fraction | |
| $CH_4$ | 0.95 |
| $C_2H_6$ | 0.02 |
| $C_3H_8$ | 0.015 |
| $n-C_4H_{10}$ | 0.01 |
| $n-C_5H_{12}$ | 0.005 |
| $CO_2$ | 0 |

TABLE 2: ELEMENTAL COMPOSITION OF BIOMASS (WT%)

| Carbon | 51.8 |
|---|---|
| Hydrogen | 6.04 |
| Nitrogen | 0.17 |
| Sulfur | 0.09 |
| Oxygen | 41.9 |
| LHV (MJ/kg) (5% wet) | 18.06 |

Biomass gasification part is briefly described below. Complete details of syngas generation from biomass is given in our previous publication [3]. Wet biomass is dried and pretreated before entering the gasifier. Here the illustrative example of an oxygen entrained flow gasifier (EFG) is utilized with subsequent cleaning of the generated syngas to remove $H_2S$, dust, soot, etc. EFG technology is a suitable technology to produce fuel due to the high gasification temperature (1600 °C) which results in relatively clean and tar-free syngas [4]. The hot and reactive syngas out of the gasifier is quenched in a waste heat boiler (WHB) to a temperature where the gas is chemically stable and the shift towards production of $CO_2$ is not favored. The syngas then enters a water-wash unit to be cleaned of particles and ammonia before entering the acid gas removal unit. The main purpose of this unit is to remove $H_2S$. However, it is assumed that 5% $CO_2$ is co-absorbed with $H_2S$ and taken out of the process. The differentiating feature of the proposed designs is the natural gas reforming step.

The methanol reactor is simulated here assuming equilibrium is reached at reactor outlet. Methanol synthesis involves the following three reactions:

$$2H_2+CO \rightarrow CH_3OH$$

$$3 H_2+CO_2 \rightarrow CH_3OH+H_2O$$

$$H_2O+CO \rightarrow CO_2+H_2$$
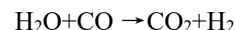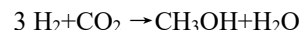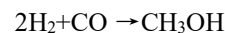
The syngas composition at the reactor inlet is particularly important for the rate of reaction as well as product selectivity and must be such that the M ratio is slightly above 2:

$$\mathbf{M}= \frac{[H_2]-[CO_2]}{[CO]+[CO_2]}$$

In a conventional BTL process, **M** is adjusted by using a Water Gas Shift (WGS) reactor, to shift CO and steam to $CO_2$ and $H_2$, followed by a $CO_2$ separation unit. However, in the proposed designs, use of WGS is avoided in order to minimize loss of carbon as $CO_2$.

### A. Design 1: Biomass gasification with ATR+SOEC

In the first design (Fig. 1), an autothermal reformer (ATR) is used to generate syngas, while the $O_2$ required for both biomass gasification and natural gas reforming is provided by a solid oxide electrolysis cell (SOEC). Pre-reforming is used upstream of the ATR to prevent coke formation on the ATR catalyst by converting almost all higher hydrocarbons to methane and carbon oxides. The SOEC produces just enough $O_2$ and $H_2$ for the process.
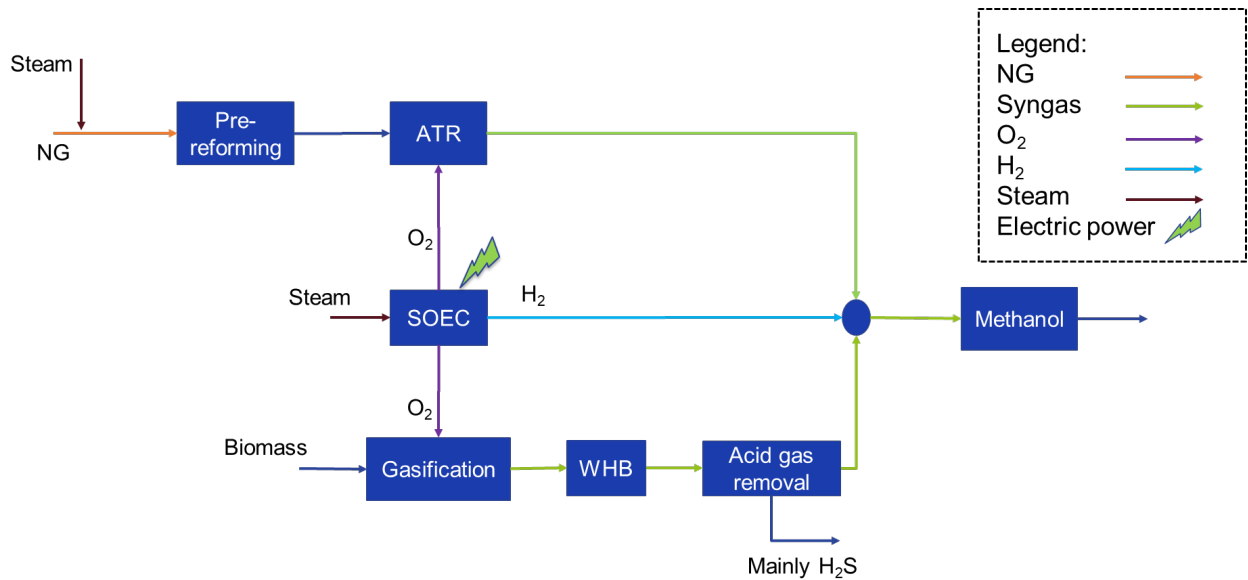
Figure 1: Block flow diagram of design 1

## B. Design 2: Biomass gasification with ATR/GHR

In the second design (Fig. 2), the gasification section is the same as design 1, but the natural gas reforming section is different. Natural gas is sent to a gas-heated-reformer (GHR) followed by an ATR. The heat required in the GHR is provided by the exhaust stream from the ATR; this approach efficiently uses the high temperature exergy of the exhaust stream. Gas heated reformer (GHR) is basically a shell and tube heat exchanger, with catalyst inside the tubes [5].

The gas heated reformer (GHR) eliminates the need for an externally fired primary reformer. Although the reformed gas has high hydrogen content, when mixed with the synthesis gas from biomass gasification, the extra hydrogen is not enough to raise the stoichiometric number required for methanol synthesis. Therefore, a fraction of the reformed gas is sent to a water gas shift (WGS) reactor and a $CO_2$ separation unit. An important synergy here is that gasification syngas also needs to be cleaned of acid gas, mainly $H_2S$, therefore they will share the same syngas cleaning unit and there is no need for a separate $CO_2$ separation unit which is an important cost saving.

## IV. RESULTS

The results are compared to a conventional biomass to methanol (BTL) process where part of the gasification syngas is sent to a WGS reactor and $CO_2$ separation unit to adjust the stoichiometric number before the methanol reactor. The thermal input from natural gas and biomass are kept constant at 134.1 MW in all designs. The thermal efficiency is calculated based on the thermal flow with the assumption that conversion of thermal power to electrical power has an efficiency of 50%. The results of Table 3 show that both proposed designs have lower $CO_2$ process emissions than the conventional BTL process. Design 1 has the highest carbon efficiency (89%) but is more expensive than design 2 and is heavily dependent on renewable electricity. Design 1 produces more methanol than design 2 with an increase in specific cost of only 8%. BTL is the most expensive with highest process $CO_2$ emissions, which however are from "carbon-neutral" sources.

Carbon and energy flows (thermal) provide interesting insights about the proposed designs (Fig. 2 and Fig. 3).
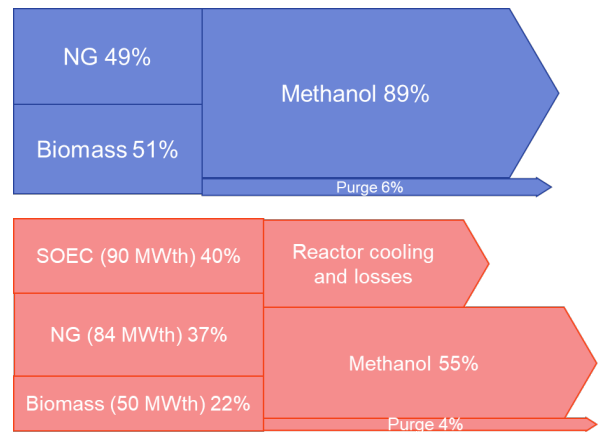


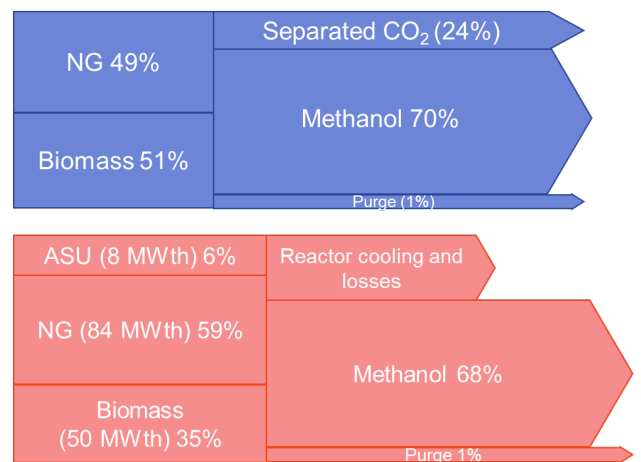Figure 2: Carbon (top) and thermal Energy flows (bottom) of design 1



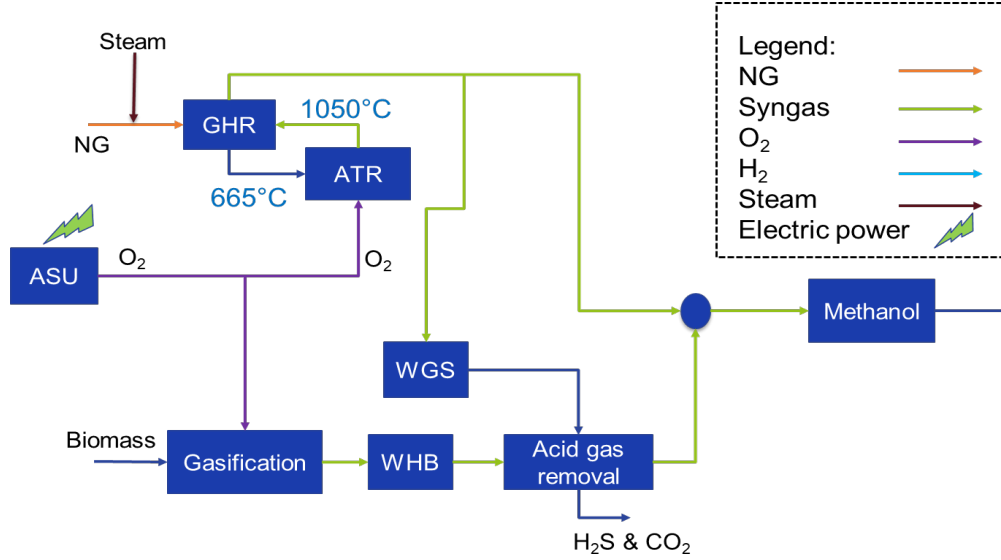Figure 3: Carbon (top) and thermal Energy flows (bottom) of design 2

Figure 4: Block flow diagram of design 2

Table 3: Technical comparison of proposed concepts

|  | Design 1 SOEC | Design 2 ATR/GHR | BTL |
|---|---|---|---|
| NG capacity (MWth) | 84.1 | 84.1 | 0 |
| Biomass capacity (MWth) | 50 | 50 | 134.1 |
| Methanol production (ton/hr) | 22.4 | 17.6 | 15.2 |
| Power in SOEC (MW) | 45 | 0 | 0 |
| Carbon efficiency (%) | 89 | 70 | 44 |
| Energy efficiency (%) | 55 | 68 | 58 |
| Purchased equipment cost (M$) | 113 | 82 | 122 |
| Process $CO_2$ emissions (ton $CO_2$/ton MeOH) | 0.12 | 0.53 | 1.62 |

## V. COST ESTIMATION

Equipment price data and methods to adjust those based on capacity are important in making reliable cost estimates. The purchased equipment cost can be estimated based on sizing and reference data. By knowing the purchased cost of a reference unit ($C_{ref}^{unit}$) and its size ($A_{ref}$), the size-adjusted cost ($C^{unit}$) is calculated by:

$$C^{unit} = C_{ref}^{unit} \times \left(\frac{A^{unit}}{A_{ref}}\right)^k \times \left(\frac{CEPCI_{current}}{CEPCI_{ref}}\right) \quad (1)$$

In order to update the capital cost from the reference year to the current values ($2020), the Chemical Engineering Plant Cost Index (CEPCI) is used. A scaling factor (k) between 0.6-0.85 is used depending on the scalability of each piece of equipment.

The fixed capital investment (FCI) and total capital investment (TCI) for the project are estimated based on the Percentage of Delivered Equipment Cost method [6] as shown in (2). $E_i$ is the delivered cost of equipment $i$ and is assumed to be 10% of the purchased equipment cost ($C^{unit}$). Multipliers $f_1$, $f_2$, $f_3$, …, $f_n$ are multiplying factors for piping, electrical, indirect costs, etc. The ratios used are suited for Solid-fluid processing plants [6].

$$FCI_i = E_i \sum (1 + f_1 + f_2 + \cdots + f_n) \quad (2)$$

$$FCI = \sum FCI_i \quad (3)$$

$$TCI = FCI + WC \quad (4)$$

A summary of the purchased equipment cost is given in Table 4.

Table 4: Purchased equipment cost (M$)

|  | Design 1 SOEC | Design 2 ATR/GHR | BTL |
|---|---|---|---|
| Pre-treatment | 7.4 | 7.4 | 22.5 |
| Gasification | 17.9 | 17.9 | 67.5 |
| Gas cleaning | 6.3 | 6.3 | 4.7 |
| Syngas processing (Compressors, Selexol unit & WGS reactor) | 4.1 | 11.2 | 18.7 |
| MeOH production | 11.8 | 10.1 | 9.2 |
| Electrolyser (including replacements) | 60.4 | 0.0 | 0.0 |
| Reforming | 5.1 | 29.0 | 0.0 |
| **Total (M$)** | **112.9** | **81.8** | **122.5** |

Economic analysis is performed based on the Levelized Cost approach to compare the cost competitiveness of proposed designs relative to the conventional BTL. The unit production cost of methanol is calculated by (LCOMeOH) ($/ton):

$$LCOMeOH = \frac{FCI \times CRF + C_{Opt}}{P_{MeOH}} \quad (5)$$

$P_{MeOH}$ is the annual production rate of methanol and $C_{Opt}$ is the annual operating cost, which is divided into feedstock and non-feedstock (biomass, natural gas and electricity):

$$C_{Opt} = C_{Opt\_feedstock} + C_{Opt\_nonfeedstock} \quad (6)$$

$$C_{Opt\_feedstock} = C_{Biomass} + C_{Electricity} + C_{Natural\ Gas} \quad (7)$$

$$C_{Opt\_nonfeedstock} = 0.05 * CAPEX \qquad (8)$$

CAPEX is considered to be the overnight investment cost for building the plant and does not include costs for interest during construction or working capital [7]. The non-feedstock operating cost is declared as an annual percentage of CAPEX which is 5% [7]. This includes co-feeds, labor, feedstock-associated costs on-site, maintenance, and by-product disposal [7]. In order to take into account the depreciation of the investment, Capital Recovery Factor (CRF) is used. When multiplied by the fixed capital investment (FCI), annualized depreciation cost of the invested capital is estimated:

$$CRF = \frac{i*(i+1)^n}{(i+1)^n - 1} \qquad (9)$$

where $i$ is the interest rate and $n$ is the plant lifetime.
The main economic parameters for evaluating LCOMeOH are shown in Table 5. The base assumption for the SOEC system is an installed cost of 1000 $/kW(el) with a lifetime of 5 years [4]. Fig. 5 shows the LCOMeOH for different designs. Both proposed designs have lower levelized cost than the BTL process (5% and 30% for design 1 and design 2, respectively).

Table 5: MAIN PARAMETERS FOR ECONOMIC ANALYSIS

| Economic parameter | Value |
|---|---|
| Plant lifetime (years) | 25 |
| Interest rate (%) | 10 |
| Annual operating hours (hr/yr) | 8000 |
| Capital recovery factor (%) | 11.0 |
| Average electricity price ($/MWh) | 100 |
| Cost of biomass (5% wet) ($/dry ton) | 50 |
| Natural Gas price ($/GJ) | 5 |
| SOEC investment cost ($/kW) | 1000 |

Electricity price has a major impact on the LCOMeOH of design 1 as shown in Fig. 6. The Figure shows that when free electricity is available, both designs produce methanol which is 30% cheaper than the conventional BTL process.
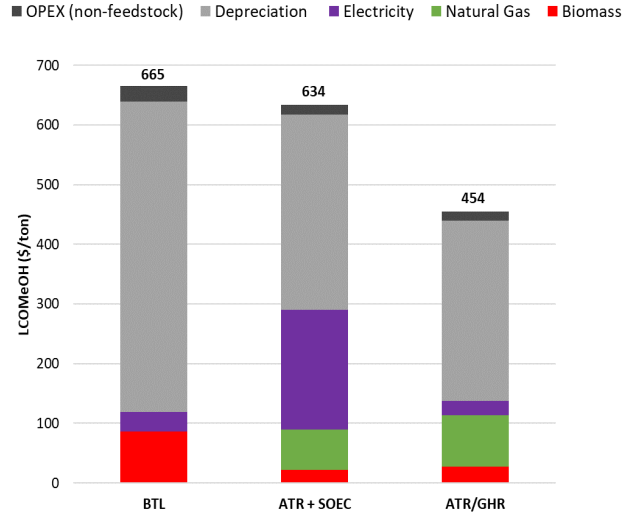


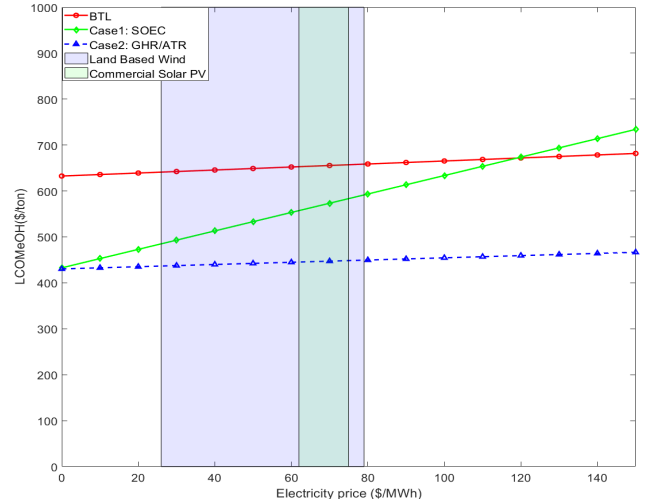Figure 5: Levelized cost of methanol for different designs



Figure 6: Levelized cost of methanol (LCOMeOH) as a function of electricity price. Main assumptions are the installed cost of SOEC of 1000 $/kW and natural gas price of 5 $/GJ.

## VI. HEAT ANALYSIS

To get a better picture of the amount of heating and cooling requirements in the proposed designs, the energy composite curves are shown in Fig. 7 and Fig. 8. In design 1, Fig. 7, there is no need for any external heating and there is 42 MW of excess heat available. Similarly, in design 2, Fig. 8, no external heating is needed while there is 34 MW excess heat. The horizontal hot line at 250°C corresponds to the steam generated during cooling of the methanol reactors. As can be observed, in both processes a large amount of excess heat is available mainly below 200°C which can be utilized for preheating or be upgraded via heat pumps.

Figure 7: Composite curves-design 1



Figure 8: Composite curves for design 2

## VII. Conclusions

Biomass is a renewable resource which holds great promise to be part of the energy mix as a renewable carbon source for production of low-carbon fuels. In this work, improvements of the carbon efficiency and profitability of biomass to liquid (BTL) process are achieved by parallel integration of natural gas reforming and biomass gasification in two different designs. This integration approach, increases the economic and environmental appeal of fuel production from biomass with a decrease in the methanol production cost by 5-30%, and the process $CO_2$ emissions decreased by 65-90% compared to a conventional BTL process. Moreover, flexibility is increased and the natural gas acts as a swing fuel. While the produced methanol includes some fossil carbon, the synergy of this integration and added flexibility increases the economic viability of deployment of biomass-based fuel production.

## Definitions and abbreviations

ASU: Air Separation Unit

BTL: Conventional Biomass to Liquid (i.e., Methanol) Process

CRF: Capital Recovery Factor

FCI: Fixed Capital Investment

LCOMeOH: Levelized Cost of Methanol

LHV: Lower Heating Value

NG: Natural Gas

SOEC: Solid Oxide Electrolysis Cell

TCI: Total Capital Investment

WC: Working Capital

WGS: Water Gas Shift reaction

WHB: Waste Heat Boiler

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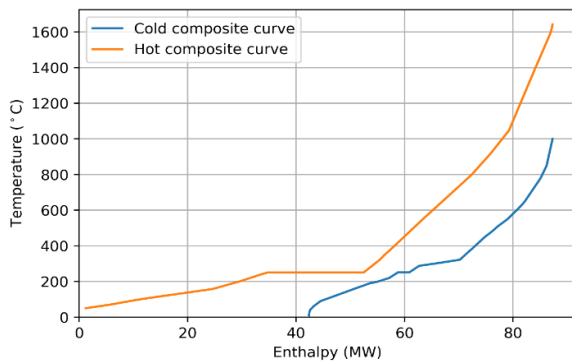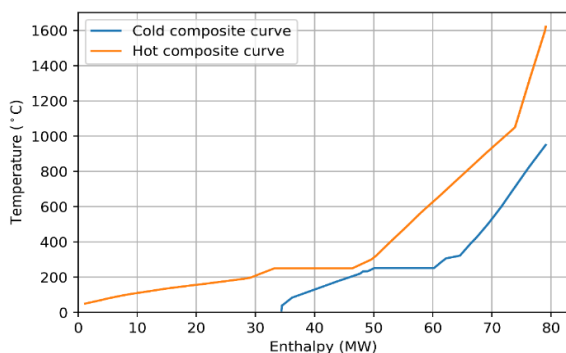[7] IRENA and Methanol Institute, Innovation Outlook: Renewable Mini-Grids. Abu Dhabi: International Renewable Energy Agency, 2021.